IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

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| **TJIOE et al** | Atty. Ref.: **4662-317** |
| Serial No. **10/522,418** | Group: **1624** |
| Filed: **October 17, 2005** | Examiner: **Balasubramanian** |

For: **PROCESS FOR THE PRODUCTION OF MELAMINE**

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

## FACTUAL DECLARATION UNDER RULE 132

Sir:

Pursuant to 37 CFR §1.132, the undersigned, **Tjien TJIOE**, hereby declares and states:

1. I am a named co-inventor of the invention described and claimed in the above-identified US Serial No. 10/522,418 filed October 17, 2005 ("the '418 application") and for all times relevant to the facts stated herein have been an employee of DSM N.V. ("DSM").

2. I have studied Chemical Engineering at the Technical University of Delft, where I received my Ph.D in 1987. As part of my employment with DSM from 1987 until about 1997 I have been working primarily on studies related to physical and chemical properties of crystals and solids. While still employed at DSM from 1997 until the present, I have been working on melamine production processes, including studies related to melamine crystallization and precipitation, as well as to coupling of melamine and urea processes.

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3. In addition to the '418 application, I am co-inventor of numerous inventions described in many granted US patents and pending US patent applications in the field of melamine and/or urea processes, namely US Patent Nos. 7,361,217; 7,094,927; 6,664,392; 6,706,856; 7,045,623; 4,806,323; 6,235,902; 6,268,459; 6,274,731; 6,262,261; 6,548,669; US 6,166, 204; and 6,579,980 as well as pending US application Serial Nos. 11/919,991 filed May 15, 2006 and 12/306,684 filed June 22, 2007.

4. Based on my education and experiences to date, I believe I am a person of much greater than ordinary skill in the art of melamine processing technologies.

5. On information and belief, the Examiner of the '418 application has cited US Patent No. 6,355,797 to Coufal et al ("Coufal et al") to reject the pending claims therein and has asserted that Coufal et al teaches mixing of two melamine-containing streams from different melamine production processes.

6. One purpose of this Declaration is to rebut the Examiner's assertion and establish that an ordinarily skilled person would not have considered it obvious to mix two melamine containing flows from two different processes for making melamine, specifically a first melamine containing flow made from a low-pressure gas phase process for the preparation of melamine from urea and a second melamine-containing flow made from a high-pressure liquid-phase process for the preparation of melamine from urea as defined by the claims of the '418 application.

7. It is well-known to the skilled person that impurities have an unpredictable and disturbing effect on crystallization and precipitation processes. In this regard, Ullmann's Encyclopedia of Industrial Chemistry (Chapter: Crystallization and Precipitation by John W. Mullin, Article Online Posting Date: January 15, 2003) (the relevant portions of which are attached as Exhibit A) observes:



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> *"The morphological development of a precipitate is a complex combination of a variety of processes including nucleation, habit modification, phase transformation, ripening, and agglomeration. The most influential system parameters are supersaturation and the concentration of active impurities...".* (emphasis added)

8. Melamine crystallization and precipitation process designs are based on experience and can be only operated and controlled within a relatively small window of composition and process parameters so as to obtain acceptable ("on-specification") product. Thus, if the amount of impurities is outside the operating window, the process gets out of control and which in turn results in unacceptable ("off-specification") product being made.

9. Combining melamine-containing flows from two different processes for making melamine means that the amount and composition of the impurities in the respective flows will change and that the composition of the combined stream of melamine-containing flows will then be outside the original operating window for each of the respective melamine-production processes. Kirk Othmer Encyclopedia of Chemical Technology (Chapter: Crystallization by Joachim Ulrich, Article Online Posting Date: August 16, 2002) (the relevant portions of which are attached as Exhibit B) cautions that:

> *"Strict protocols should be followed in operating units upstream from a crystallizer to minimize the possibility of such occurrences. Equally important is monitoring the composition of recycle streams to prevent possible accumulation of impurities."*

10. Thus, the ordinarily skilled person in the art of melamine production is well aware that the introduction of "strange" components into a melamine-containing flow is strictly undesirable. This is especially true for combining a melamine-containing stream from a low-pressure gas-phase process with a melamine-containing

stream from a high-pressure liquid-phase process as is defined by the pending claims in the '418 application, since the composition and amount of the impurities in such streams differ substantially one from the other.

11. I have read and am familiar with Coufal et al. Specifically, Coufal et al describes a cooling process for melamine melt using, amongst others, solid melamine. There is however no description in Coufal et al of the source of the solid melamine that is used as the cooling medium. The purpose of the addition of solid melamine according to Coufal et al is for cooling the melamine or for serving as crystallization nuclei. From a processing viewpoint, it would be self-evident that the most convenient way to obtain the solid melamine cooling medium is to use solid melamine from the same process that makes the melamine melt to be cooled.

12. As a person of greater than ordinary skill in the melamine production art and an understanding the purpose of the description of Coufal et al, it is therefore my conclusion that the most likely source for the solid melamine employed as the cooling medium or as a crystallization nuclei that is disclosed therein is the same process which makes the melamine melt intended to be cooled. That is, the melamine melt to be cooled and the solid melamine which serves as the cooling medium or crystallization nuclei must be obtained from the same production process according to Coufal et al. This conclusion is thus based not only because of ease of processing but otherwise the issues described previously in the cited publications above would ensue.

13. It is further noted that, in column 3, lines 1-5 of Coufal et al, the formation of new solid melamine particles in the fluidized bed is described and no solid melamine needs to be fed. This description in Coufal et al further underscore my conclusion that Coufal et al does not teach or suggest to combine two streams from two different processes for making melamine from urea, let alone to

combine melamine-containing streams made respectively from a low-pressure gas phase process for the preparation of melamine from urea and a high-pressure liquid-phase process for the preparation of melamine from urea as defined by the claims of the '418 application.

14. The ordinarily skilled person would therefore not consider it obvious based on Coufal et al to combine melamine-containing streams made respectively from a low-pressure gas phase process for the preparation of melamine from urea and a high-pressure liquid-phase process for the preparation of melamine from urea. In fact, the ordinarily skilled person would be cognizant that such streams should not be mixed together for the reasons discussed previously.

15. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully Submitted,

February 6, 2009
Date Signed

Tjien TJIOE

Ullmann



### 8.3.2. Agglomeration

Small particles in liquid suspension tend to agglomerate into clusters. A theoretical basis for the rate of agglomeration of colloidal particles in suspension was first proposed by SMOLUCHOWSKI [89]. Two types of behavior may be distinguished: *perikinetic* (static fluid with particles in Brownian motion) and *orthokinetic* (agitated dispersions), which can both be important in precipitation processes. In agitated precipitators, orthokinetic agglomeration becomes more important as the particle size and the shear rate increases.

Double-layer repulsion forces and van der Waals attraction forces operate independently in disperse systems. Repulsion forces decrease exponentially over a distance corresponding to the thickness of the ionic double layer, whereas attraction forces decrease, over a larger distance from the particle surface, as an inverse power of the distance. Consequently, attraction normally predominates at very small and very large distances, and repulsion over intermediate distances [90].

The assessment and modeling of agglomeration kinetics in precipitation processes are discussed in [5], [91], [92].

### 8.3.3. Precipitate Morphology

The morphological development of a precipitate is a complex combination of a variety of processes including nucleation, habit modification, phase transformation, ripening, and agglomeration. The most influential system parameters are supersaturation and the concentration of active impurities, although pH can also exert a profound effect in some aqueous systems.

The dominant influence of supersaturation on the particle-size characteristics of a precipitate has been summed up in the so-called Weimarn laws of precipitation [93] which, while open to theoretical criticism, provide very useful guidelines for batch precipitation behavior. They are illustrated in Figure 38:

1) As the concentration of reactants increases, the median particle size of the precipitate (determined at a given time after mixing the reactants) increases to a maximum and then decreases. As the time interval increases, the maximum is displaced to lower initial supersaturation and higher median particle size.
2) For a completed precipitation, the median size of the precipitate crystals decreases as the initially created supersaturation $S$ is increased.

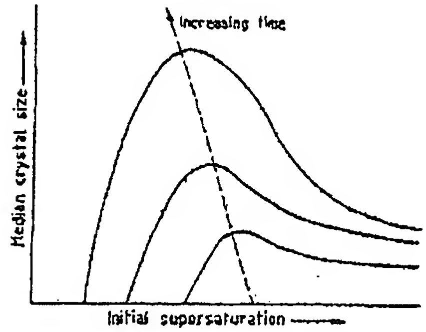


Figure 38. Illustration of Weimarn's laws of precipitation

For a given system, maximum agglomeration often appears to occur at a certain level of supersaturation; this behavior has been linked to the character of the adsorption layer surrounding a growing crystal which consists of loosely bonded, partially integrated groups of the crystallizing species [7].

An oversimplified but graphic example of the interactive effects of supersaturation, nucleation, and growth in the development of precipitated particles is given by WALTON [94], who considered the homogeneous nucleation of three different systems at an arbitrary value of supersaturation $S = 100$ (Eq. 2). If the number of particles nucleated is $10^6/cm^3$, the maximum precipitated particle sizes expected for three different solubilities $c*$ of $10^{-7}$, $10^{-4}$, and $10^{-1}$ mol/L, were concluded to be 1, 10, and 100 µm, respectively.

Alternatively, the approximate particle size can be estimated if the above three solutions are all assumed to have the same concentration, e.g., 1 mol/L. The first ($S = 10^7$) would nucleate homogeneously, forming approximately 1-nm particles and producing a colloidal system (gel) which could remain stable for long periods before the primary particles agglomerated. The second ($S = 10^4$) would also nucleate homogeneously, forming primary particles

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The screw dislocation theory (41), often referred to as the BCF theory (after its formulators Burton, Cabrera, Frank), shows that the dependence of growth rate on supersaturation can vary from a quadratic relationship at low supersaturation to a linear relationship at high supersaturation. In the BCF theory, growth rate is given by

$$G = C\left(\frac{\varepsilon s^2}{\sigma_1'}\right)\tanh\left(\frac{\sigma_1'}{\varepsilon s}\right) \tag{22}$$

where $\varepsilon$ is screw dislocation activity and $\sigma'_1$, is a system-dependent quantity that is inversely proportional to temperature. The dependence of growth rate on supersaturation is linear if the ratio $\sigma_1/\varepsilon s$ large, but the functional dependence becomes parabolic as the ratio becomes small. This is because $(\frac{\sigma_1'}{\varepsilon s}) \longrightarrow \frac{\sigma_1'}{\varepsilon s}$ as $\frac{\sigma_1'}{\varepsilon s}$ becomes small (supersaturation becomes large), and $(\frac{\sigma_1'}{\varepsilon s}) \longrightarrow 1.0$ as $\frac{\sigma_1'}{\varepsilon s}$ becomes large (supersaturation becomes small). It is thus possible to observe variations in the dependence of growth rate on supersaturation for a given crystal–solvent system.

An empirical approach can also be used to relate growth kinetics to supersaturation with a power-law function of the form

$$G = k_G s^g \tag{23}$$

where $k_G$ and g are constants determined by fitting the equation to growth-rate data. Such an approach should be valid over small ranges of supersaturation, and analysis of the theories discussed above shows that the more fundamental equations can be fit by equation 23 over limited ranges of supersaturation. For example, using the empirical approach to describe systems in which the screw dislocation model was applicable would limit $g$ to values between 1 and 2, assuming $\epsilon$ was independent of supersaturation.

All the models described above indicate the importance of system temperature on growth rate. Dependencies of growth kinetics on temperature are often expressed in terms of an Arrhenius expression:

$$k_G = k_G^0 \exp\left(-\frac{\Delta E_G}{RT}\right) \tag{24}$$

where $k_G$ is a growth rate coefficient of the type required in equation 23, $K_G{}^0$ is a constant, and $\Delta E_G$ is an activation energy. The magnitude of $\Delta E_G$ can be as large as that for many chemical reactions, 42 kJ/mol (>10 kcal/mol).

Both supersaturation and temperature can have different effects on the growth rates of different faces of the same crystal. Such occurrences have implications with respect to crystal habit, and these are dealt with in a later section.

*Effects of Impurities and Solvent.* The presence of impurities usually decreases the growth rates of crystalline materials, and problems associated with the production of crystals smaller than desired are commonly attributed to contamination of feed solutions. Strict protocols should be followed in operating units upstream from a crystallizer to minimize the possibility of such occurrences. Equally important is monitoring the composition of recycle streams

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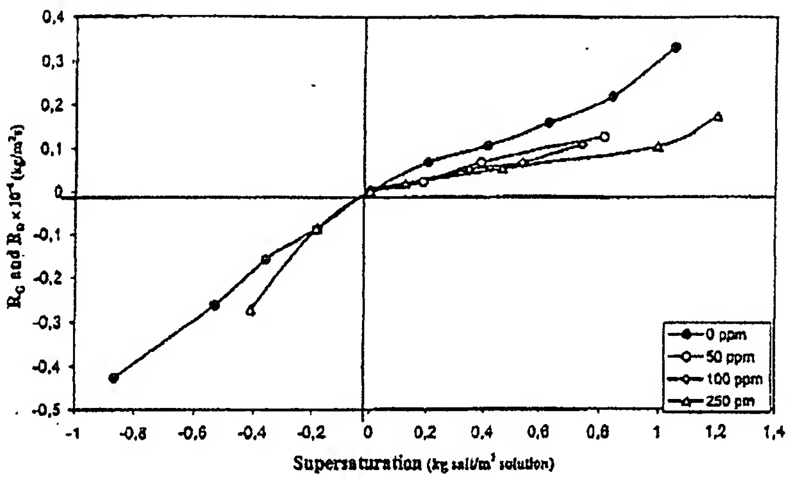


**Fig. 9.** Growth and dissolution rates of NaCl in the presence of $MgCl_2$ [(of different amounts (0–250 ppm)] after correction of the saturation (kinetic effect) (47).

to prevent possible accumulation of impurities. Furthermore, crystallization kinetics used in scaleup should be obtained from experiments on solutions as similar as possible to those expected in the full-scale process.

Figures 9 and 10 (47) show that $MgCl_2$ reduces the growth rate of NaCl. The reduction is stronger with increasing amounts of $MgCl_2$ (see Fig. 9 the kinetic effect). This is, however, only clear after a correction in the saturation point.

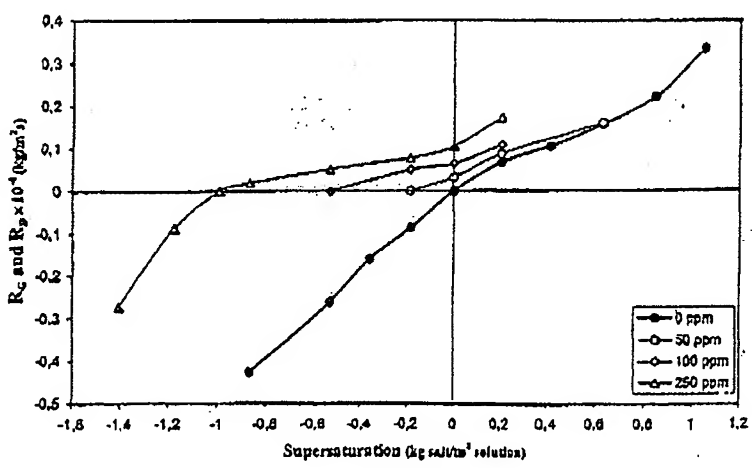


**Fig. 10.** Growth and dissolution rates of NaCl in the presence of $MgCl_2$ of different amounts (0–250 ppm) (thermodynamic effect) (47).